FORM PTO-1390 (REV 10-95) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. §371

ATTORNEY'S DOCKET NUMBER: ATOCM 241

U.S. APPLICATION NO. (If known, see 37 CFR §1.5): 10/018829

INTERNATIONAL APPLICATION NO.	INTERNATIONAL FILING DATE	PRIORITY DATE CLAIMED
PCT/FR00/01760	23 JUNE 2000	28 JUNE 1999

TITLE OF INVENTION: CORROSION INHIBITING COMPOSITIONS FOR HEAT TRANSFER FLUIDS

APPLICANT(S) FOR DO/EO/US: VALOT, Emeryc, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ■ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. §371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1).
4. ■ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ■ A copy of the International Application as filed (35 U.S.C. §371(c)(2))
   a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
   b. ■ has been transmitted by the International Bureau.
   c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ■ A translation of the International Application into English (35 U.S.C. §371(c)(2)).
7. ■ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3))
   a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
   b. ☐ have been transmitted by the International Bureau.
   c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
   d. ■ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. §371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 C.F.R. §§1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 C.F.R. §§3.28 and 3.31 is included.
13. ■ A FIRST preliminary amendment.
    ☐ A SECOND or SUBSEQUENT preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☐ Other items or information:

U.S. APPLICATION NO. (if known, see 37 CFR §1.5)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
10/018829	PCT/FR00/01760	ATOCM 241

17. ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR §1.492 (a) (1) - (5)):

		CALCULATIONS PTO USE ONLY
Search Report has been prepared by the EPO or JPO	$890.00	
International preliminary examination fee paid to USPTO (37 CFR §1.482)	$710.00	
No international preliminary examination fee paid to USPTO (37 CFR §1.482) but international search fee paid to USPTO (37 CFR §1.445(a)(2))	$740.00	
Neither international preliminary examination fee (37 CFR §1.482) nor international search fee (37 CFR §1.445(a)(2)) paid to USPTO	$1040.00	
International preliminary examination fee paid to USPTO (37 CFR §1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)	$100.00	

ENTER APPROPRIATE BASIC FEE AMOUNT =	$890.00	
Surcharge of **$130.00** for furnishing the oath or declaration later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 C.F.R. §1.492(e)).		

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	27 - 20 =	7	x $ 18.00	$126.00	
Independent claims	3 - 3 =	0	x $ 84.00	$0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ $ 280.00		
TOTAL OF ABOVE CALCULATIONS =				$1,016.00	
Reduction of 1/2 for filing by small entity, if applicable. A Verified Small Entity Statement must also be					
SUBTOTAL =				$1,016.00	
Processing fee of **$130.00** for furnishing the English translation later than ☐ 20 ☐ 30 months from the earliest claimed priority date (37 C.F.R. §1.492(f)).					
TOTAL NATIONAL FEE =				$1,016.00	
Fee for recording the enclosed assignment (37 C.F.R. §1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 C.F.R. §§3.28, 3.31). $40.00 per property.					
TOTAL FEES ENCLOSED =				$1,016.00	
				Amount to be refunded:	
				charged:	

a. ■ A check in the amount of $1,016.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. 13-3402 in the amount of $ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. ■ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 13-3402. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 C.F.R. §§1.494 or 1.495 has not been met, a petition to revive (37 C.F.R. §1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO: Customer Number 23,599

23599
PATENT TRADEMARK OFFICE

Filed: 21 DECEMBER 2001
IWM:kmo

SIGNATURE

I. William Millen
NAME

19,544
REGISTRATION NUMBER

APPLICATION DATA SHEET

APPLICATION INFORMATION

Application Type::	REGULAR
Subject Matter::	UTILITY
CD-ROM or CD-R?::	NONE
Title::	CORROSION INHIBITING COMPOSITIONS FOR HEAT TRANSFER FLUIDS
Attorney Docket Number::	ATOCM 241

INVENTOR INFORMATION

Applicant Authority Type::	INVENTOR
Primary Citizenship Country::	France
Status::	FULL CAPACITY
Given Name::	Emeryc
Family Name::	VALOT
City of Residence::	Viroflay
Country of Residence::	France
Street of Mailing Address::	4, rue Sainte-Genevieve
City of Mailing Address::	Viroflay
Country of Mailing Address::	France
Postal or Zip Code of Mailing Address::	F-78220

DOMESTIC PRIORITY INFORMATION

Application::	Continuity Type::	Parent Application::	Parent Filing Date::
This Application	National Stage of	PCT/FR00/01760	06/23/00

FOREIGN PRIORITY INFORMATION

Application Number::	Country::	Filing Date::	Priority Claimed::
99/08214	France	06/28/99	YES

ASSIGNMENT INFORMATION

Assignee Name::	ATOCHEM S.A.
Street of Mailing Address::	4/8, cours Michelet
City of Mailing Address::	Puteaux
Country of Mailing Address::	France
Postal or Zip Code of Mailing Address::	F-92800

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of :

Emeryc Valot — Group Art Unit: Unassigned

Serial No.: Unassigned — Examiner: Unassigned

Filed: Herewith

For:

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to initial examination, please amend the above-identified application as follows:

IN THE CLAIMS:

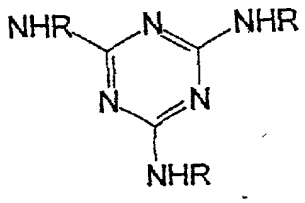
Please amend the claims as follows:

1. (Amended) A process for inhibiting multimetal corrosion by at least one heat transfer fluid, comprising introducing, into said fluid, 3 to 6% by weight of a system of organic inhibitors comprising:

- (I) 5 to 15% by weight of at least one of an unsaturated monocarboxylic acid comprising 10-18 carbon atoms or of at least one alkali metal salt thereof, of at least one amine salt thereof, the amine being monoethylamine, diethylamine or triethylamine, or at least one alkanolamine salt thereof, the alkanolamine being monoethanolamine, diethanolamine, triethanolamine or methyldiethanolamine or mixture thereof,
- (II) 40 to 70% by weight of at lest one of a saturated carboxylic acid from the group consisting of a saturated monocarboxylic acid comprising 5-16 carbon atoms, a saturated dicarboxylic acid comprising 4-12 carbon atoms, and an alkali metal or amine or

alkanolamine salt of said acids;

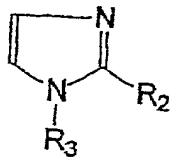
- (III) 20 to 40% by weight of a tricarboxylic derivative of 1,3,5-triazine corresponding to the formula



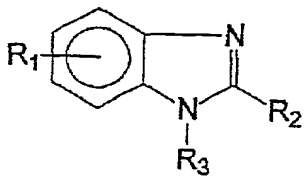
In which formula R is a carboxylic group comprising 2-6 carbon atoms, or an alkali metal or amine or alkanolamine salt thereof,

(IV) 1 to 5% by weight of an azole derivative comprising at least one member from the group consisting of:

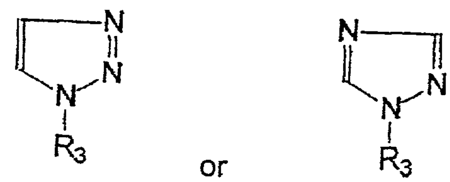
(a) an imidazole of formula



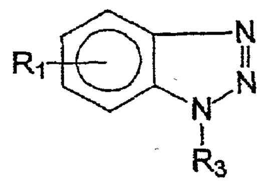
(b) a benzimidazole of formula



(c) a triazole of formula

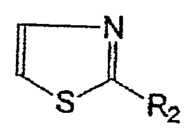


(d) a benzotriazole of formula

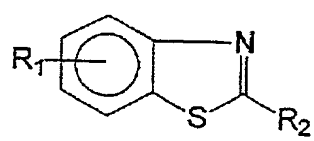


(e) tetrahydrobenzotriazole

(f) a thiazole of formula



(g) a benzothiazole of formula

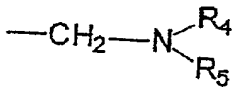


(h) and an alkali metal salt of these azole derivatives, in which formulae

R1 is a hydrogen atom or a methyl radical

R2 is a hydrogen atom or a mercapto radical

R3 is a hydrogen atom or a radical of formula



with R4 and R5, which are identical or different, representing a 2-ethylhexyl or hydroxyalkyl radical.

2. (Amended) A process according to Claim 1, in which the ratio by weight of components (I) and (II), (I/II), ranges from 5 to 15, and the ratio by weight of components (I) and (II) on one part and of the component (III) on the other part, (I+II/III), ranges from 1.5 to 3.

3. (Amended) A process according to Claim 1, in which the system of organic inhibitors is composed of:

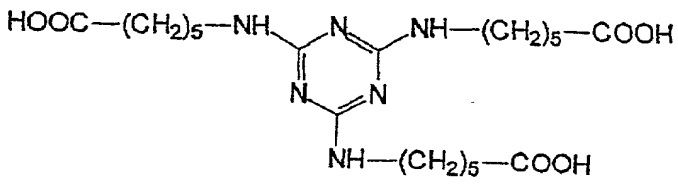
- 6 to 8% by weight of the component (I);
- 55 to 65% by weight of the component (II);
- 25 to 35% by weight of the component (III);
- 2 to 3% by weight of the component (IV).

4. (Amended) A process according to Claim 1, in which the saturated carboxylic acid is n-hexanoic acid, heptanoic acid, n-octanoic acid or nonanoic acid.

5. (Amended) A process according to Claim 1, in which the dicarboxylic acid is suberic acid, azelaic acid or sebacic acid.

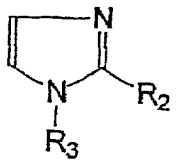
6. (Amended) A process according to Claim 1, in which the unsaturated monocarboxylic acid is undecyclenic acid.

7. (Amended) A process according to Claim 1, in which the tricarboxylic derivative of 1,3,5-triazine (III) is the compound of formula:

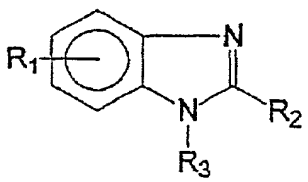


8. (Amended) A composition which inhibits multimetal corrosion composed of an aqueous solution assaying from 10 to 60% by weight of an inhibitor system composing

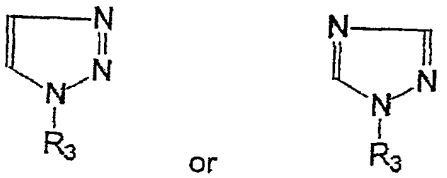
(a) an imidazole of formula



(b) a benzimidazole of formula

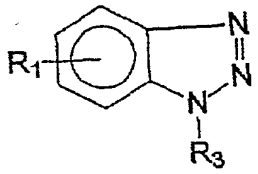


(c) a triazole of formula



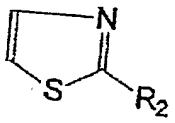
or

(d) a benzotriazole of formula

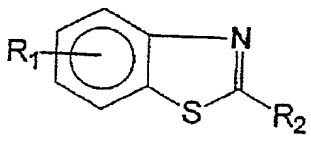


(e) tetrahydrobenzotriazole

(f) a thiazole of formula



(g) a benzothiazole of formula

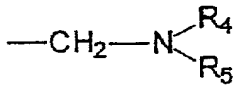


(h) and an alkali metal salt of these azole derivatives, in which formulae

R1 is a hydrogen atom or a methyl radical

R2 is a hydrogen atom or a mercapto radical

R3 is a hydrogen atom or a radical of formula



with R4 and R5, which are identical or different, representing a 2-ethylhexyl or hydroxyalkyl radical.

9. (Amended) An antifreeze composition which inhibits multimetal corrosion, comprising: corrosion, comprising:

- 0.1 to 10% by weight of the inhibiting composition according to Claim 8;
- 90 to 99.9% by weight of an aqueous/alcoholic solution having a freezing point of less and 0°C, the alcohol being from the group consisting of methanol, ethanol, 2-propanol, glycerol, ethylene glycol, diethylene glycol, propylene glycol, 1-methoxy-2-propanol, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether and ethylene glycol butyl ether.

10. (Amended) An inhibiting antifreeze composition according to Claim 9, the alcohol of which is ethylene glycol.

Please add the following new claims:

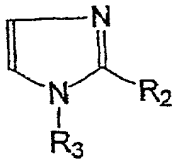
11. (New) A process according to Claim 1, comprising introducing into said at least one fluid 3.8 to 5% of said system of organic inhibitor.

12. (New) A process according to Claim 1, wherein at least one of R4 and R5 is $-CH_2-CH_2-OH$.

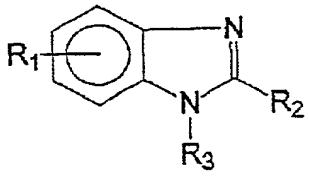
13. (New) A process according to Claim 2 wherein the ratio (I/II) is from 8 to 12 and the ratio of (I+II/III) is from 1.9 to 2.2.

14. (New) A system of organic inhibitors comprising:

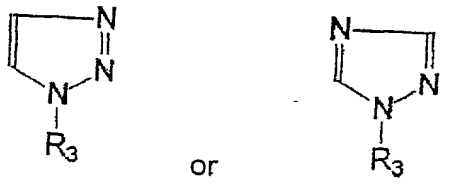
(a) an imidazole of formula



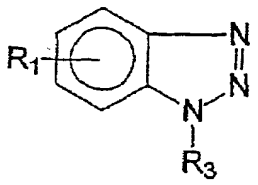
(b) a benzimidazole of formula



(c) a triazole of formula

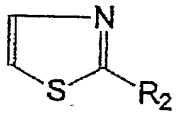


(d) a benzotriazole of formula

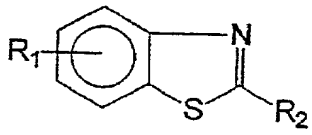


(e) tetrahydrobenzotriazole

(f) a thiazole of formula



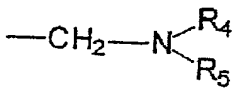
(g) a benzothiazole of formula



(h) and an alkali metal salt of these azole derivatives, in which formulae R1 is a hydrogen atom or a methyl radical

R2 is a hydrogen atom or a mercapto radical

R3 is a hydrogen atom or a radical of formula



with R4 and R5, which are identical or different, representing a 2-ethylhexyl or hydroxyalkyl radical.

15. (New) A system according to Claim 14, wherein said azole derivative comprises (a).

16. (New) A system according to Claim 14, wherein said azole derivative comprises (b).

17. (New) A system according to Claim 14, wherein said azole derivative comprises (c).

18. (New) A system according to Claim 14, wherein said azole derivative comprises (d).

19. (New) A system according to Claim 14, wherein said azole derivative comprises (e).

20. (New) A system according to Claim 14, wherein said azole derivative comprises (f).

21. (New) A system according to Claim 14, wherein said azole derivative comprises (g).

22. (New) A system according to Claim 14, wherein said azole derivative comprises (h).

23. (New) A system according to Claim 14, in which the ratio by weight of components (I) and (II), (I/II), ranges from 5 to 15, and the ratio by weight of components (I) and (II) on one part and of the component (III) on the other part, (I+II/III), ranges from 1.5 to 3.

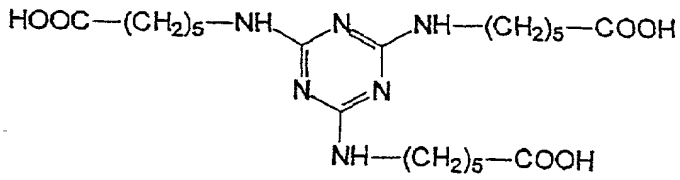
24. (New) A system according to Claim 14, in which the system of organic inhibitors is composed of:

- 6 to 8% by weight of the component (I);
- 55 to 65% by weight of the component (II);
- 25 to 35% by weight of the component (III);
- 2 to 3% by weight of the component (IV).

25. (New) A system according to Claim 14, in which the saturated carboxylic acid is n-hexanoic acid, heptanoic acid, n-octanoic acid or nonanoic acid.

26. (New) A system according to Claim 14, in which the dicarboxylic acid is suberic acid, azelaic acid and sebacic acid.

27. (New) A system according to Claim 14, in which the tricarboxylic derivative of 1,3,5-triazine (III) is the compound of formula:



REMARKS

A principal purpose of the Preliminary Amendment is to facilitate examination by removing multiple dependent claims. Other purposes are to provide claims to preferred features and claims 14-27 directed to the system of organic inhibitors.

The Commissioner is hereby authorized to charge any fees associated with this response or credit any overpayment to Deposit Account No. 13-3402.

Respectfully submitted,

I William Millen Reg. No. 19,544
Attorney for Applicant(s)

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Arlington Courthouse Plaza 1, Suite 1400
2200 Clarendon Boulevard
Arlington, Virginia 22201
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Attorney Docket No.: ATOCM-241

Date: December 20, 2001

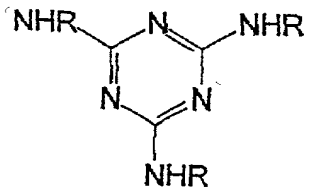
VERSION WITH MARKINGS TO SHOW CHANGES MADE

1. (Amended) ~~Process~~ A process for inhibiting multimetal corrosion by at least one heat transfer ~~fluids~~ fluid, ~~whether or not these fluids comprise an organic compound which lowers the freezing point, which consists in~~ comprising introducing, into ~~the~~ said ~~fluids~~ fluid, 3 to 6% by weight ~~and preferably 3,8 to 5%~~ of a system of organic inhibitors ~~composed of~~ comprising:

- (I) 5 to 15% by weight of at least one of an unsaturated monocarboxylic acid comprising 10-18 carbon atoms or of at least one alkali metal salt thereof, of at least one ~~of~~ ~~its~~ amine ~~salts~~ salt thereof, ~~one of its~~ of at least one amine ~~salts~~ salt thereof, the amine being ~~from the group of~~ monoethylamine, diethylamine or triethylamine, or ~~of its~~ at least one alkanolamine ~~salts~~ salt thereof, the alkanolamine being ~~from the group of~~ monoethanolamine, diethanolamine, triethanolamine or methyldiethanolamine or mixture thereof,

- (II) 40 to 70% by weight of at least one of a saturated carboxylic acid ~~taken~~ from the group ~~comprising~~ consisting of a saturated monocarboxylic ~~acids~~ acid comprising 5-16 carbon atoms, ~~and~~ a saturated dicarboxylic ~~acids~~ acid comprising 4-12 carbon atoms, ~~or~~ and an alkali metal or amine or alkanolamine salt of ~~these~~ said acids;

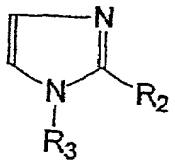
- (III) 20 to 40% by weight of a tricarboxylic derivative of 1,3,5-triazine corresponding to the formula



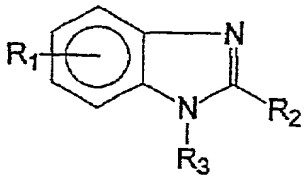
in which formula R is a carboxylic group comprising 2-6 carbon atoms, or an alkali metal or amine or alkanolamine salt ~~of this derivative~~ thereof,

(IV) 1 to 5% by weight of an azole derivative ~~taken~~ comprising at least one member from the group consisting of:

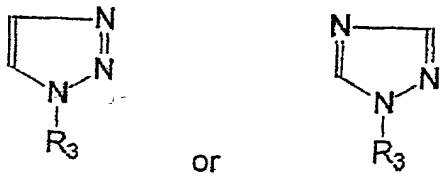
(a) an ~~imidazoles~~ imidazole of formula



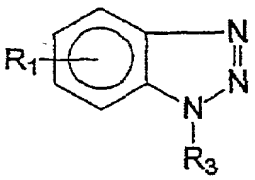
(b) a ~~benzimidazoles~~ benzimidazole of formula



(c) a ~~triazoles~~ triazole of formula

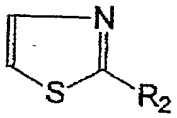


(d) a ~~benzotriazoles~~ benzotriazole of formula

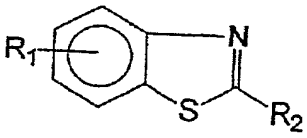


(e) tetrahydrobenzotriazole

(f) a ~~thiazoles~~ thiazole of formula



(g) a ~~benzothiazoles~~ benzothiazole of formula

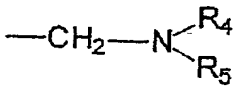


(h) and ~~the~~ an alkali metal ~~salts~~ salt of these azole derivatives, in which formulae

R1 is a hydrogen atom or a methyl radical

R2 is a hydrogen atom or a mercapto radical

R3 is a hydrogen atom or a radical of formula



with R4 and R5, which are identical or different, representing a 2-ethylhexyl or hydroxyalkyl radical ~~in a particular ethanol residue~~.

2. (Amended) ~~Process~~ A process according to Claim 1, in which the ratio by weight of components (I) and (II), (I/II), ranges from 5 to 15 ~~and, preferably from 8 to 12~~, and the ratio by weight of components (I) and (II) on one part and of the component (III) on the other part, (I+II/III), ranges from 1~~,~~.5 to 3 ~~preferably from 1,9 to 2,2~~.

3. (Amended) ~~Process~~ A process according to ~~either of Claim 1 and 2~~ Claim 1, in which the system of organic inhibitors is composed of:

- 6 to 8% by weight of the component (I);
- 55 to 65% by weight of the component (II);
- 25 to 35% by weight of the component (III);
- 2 to 3% by weight of the component (IV).

4. (Amended) ~~Process~~ A process according to ~~either of Claims 1 to 3~~ Claim 1, in which the saturated carboxylic acid is n-hexanoic acid, heptanoic acid, n-octanoic acid or nonanoic acid.

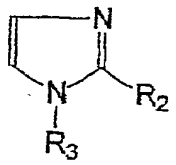
5. (Amended) ~~Process~~ A process according to ~~either of Claims 1 to 3~~ Claim 1, in which the dicarboxylic acid is suberic acid, azelaic acid and sebacic acid.

6. (Amended) ~~Process~~ A process according to ~~either of Claims 1 to 3~~ Claim 1, in which the unsaturated monocarboxylic acid is undecyclenic acid.

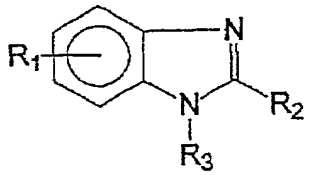
7. (Amended) ~~Process~~ A process according to ~~either of Claims 1 to 3~~ Claim 1, in which the tricarboxylic derivative of 1,3,5-triazine (III) is the compound of formula:

8. (Amended) Composition A composition which inhibits multimetal corrosion composed of an aqueous solution assaying from 10 to 60% by weight of an inhibitor system ~~as described in Claims 1 to 7~~ comprising

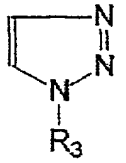
(a) an ~~imidazoles~~ imidazole of formula



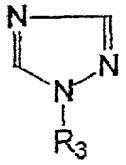
(b) a benzimidazole of formula



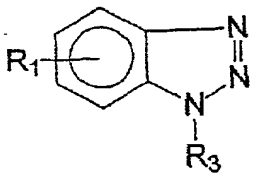
(c) a triazole of formula



or

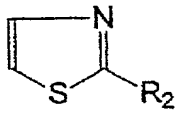


(d) a benzotriazole of formula

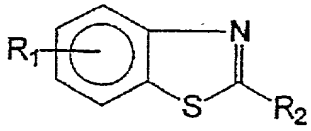


(e) tetrahydrobenzotriazole

(f) a thiazole of formula



(g) a benzothiazole of formula



(h) and an alkali metal salt of these azole derivatives, in which formulae

R1 is a hydrogen atom or a methyl radical

R2 is a hydrogen atom or a mercapto radical

R3 is a hydrogen atom or a radical of formula

with R4 and R5, which are identical or different, representing a 2-ethylhexyl or hydroxyalkyl radical.

9. (Amended) ~~Antifreeze~~ An antifreeze composition which inhibits multimetal corrosion, comprising: corrosion, comprising:

- 0.1 to 10% by weight of the inhibiting composition according to Claim 8;
- 90 to 99.9% by weight of an aqueous/alcoholic solution having a freezing point of less and 0°C ~~preferably of between -10 and -40°C~~, the alcohol being from the group consisting of methanol, ethanol, 2-propanol, glycerol, ethylene glycol, diethylene glycol, propylene glycol, 1-methoxy-2-propanol, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether and ethylene glycol butyl ether.

10. (Amended) ~~Inhibiting~~ An inhibiting antifreeze composition according to Claim 9, the alcohol of which is ethylene glycol.

Claims 11-27 have been added.

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En ce qui concerne les codes à deux lettres et autres abréviations, se référer aux "Notes explicatives relatives aux codes et abréviations" figurant au début de chaque numéro ordinaire de la Gazette du PCT.

(54) Title: CORROSION INHIBITING COMPOSITIONS FOR HEAT TRANSFER FLUIDS

(54) Titre: COMPOSITIONS INHIBITRICES DE LA CORROSION POUR FLUIDES DE TRANSFERT DE CHALEUR

(57) Abstract: The invention concerns compositions for inhibiting corrosion of various metals by heat transfer fluids consisting of a combination of an unsaturated monocarboxylic acid, a saturated monocarboxylic or dicarboxylic acid, a 1,3,5-triazine tricarboxylic derivative and an azole compound derivative. Said compositions inhibit corrosion by cavitation in particular.

(57) Abrégé: On décrit des compositions inhibitrices multimétaux de la corrosion par les fluides de transfert de chaleur qui sont constituées par l'association d'un acide monocarboxylique insaturé, d'un acide mono- ou dicarboxylique saturé, d'un dérivé tricarboxylique de la 1, 3, 5-triazine et d'un dérivé azole. Ces compositions inhibent en particulier la corrosion par cavitation.

The field of the invention is that of aqueous liquids which can be used as heat transfer fluids for cooling circuits, for example cooling circuits of internal combustion engines, the corrosiveness of which is to be overcome.

Water and aqueous solutions are very widely used as cooling fluids in circuits constructed of various metals, copper, steel, aluminium, cast iron and their alloys, which they attack as soon as the corrosion conditions are achieved. There are many corrosion factors: presence of ions, high temperatures, pressure, flow of fluids (cavitation corrosion), coupling to welds; attention should very particularly be paid to cavitation corrosion phenomena.

The first consequence of corrosion is the loss of material from the walls of the circuits and their perforation. In addition, corrosion products are formed, the deposits of which disrupt transfer of heat between the fluid and the walls of the circuit and bring about superheating on the hot walls, with high risks of failure of sensitive mechanical components.

The products used to lower the freezing point of water are a factor having a particularly serious effect on worsening the corrosiveness of cooling fluids. The use of saline brines, for the aggressiveness of which, in particular towards welds and aluminium, a satisfactory solution has never really been found, has virtually been abandoned. Industry has been won over to organic antifreezes of the class of the alcohols, methanol, ethanol, 2-propanol, glycerol, ethylene glycol, diethylene glycol, propylene glycol, ethylene glycol methyl, ethyl, propyl or butyl ether, and 1-methoxy-2-propanol. Ethylene glycol is by far the most widely used antifreeze today. Nevertheless, the problem is still posed of protecting from corrosion cooling circuits fed with aqueous fluids comprising or not comprising organic antifreezes, of developing compositions which inhibit corrosion in such media and, if possible, of formulating antifreeze compositions which are themselves inhibiting corrosion.

These compositions are burdened by specific constraints relating to environmental protection. It is forbidden, or in any case highly inadvisable, to include phosphates, nitrites, borates, molybdates and amines in combination with nitrites, which, in the prior art, had all the same been recommended and some of which had been widely used. Phosphates precipitate on contact with hard water and, for this reason, their concentration and activity decrease (depletion). It is possible to combat this, but at the price of an increase in the cost of the protection, by the use of certain additives (JP-A-62205183). In addition, these phosphates are harmful to the environment (eutrophication of water). Amines, when they are used in combination with nitrites, lead to the risk of formation of nitrosamines, which are highly toxic products. Discharges of fluids to which boron derivatives or molybdates have been added are also harmful and require treatment before they are returned to the environment. Attention has therefore been firmly directed towards other organic inhibitors, which has given rise to a great many publications and a great many patents, including, for example:

- US 819,321, cited in US 4,759,864, describing an antifreeze based on the combination of an alkylbenzoic acid (or alkylbenzoate) with a C_8-C_{12} monocarboxylic acid (or carboxylate) and triazole, with an aminophosphonic acid derivative as precipitation inhibitor and polyacrylic acid (polyacrylate) as stabilizer;
- US 4,647,392, for an antifreeze with C_5-C_{16} monocarboxylic acid (monocarboxylate), C_5-C_{16} diacid (salt) and triazole derivative;
- US 4,657,689, for an antifreeze comprising a C_5-C_{16} carboxylic acid (carboxylate), a C_5-C_{16} dicarboxylic acid (or salt), a triazole derivative and an alkaline C_{10}-C_{20} sulphonate;
- US 4,588,513, for an antifreeze with dicarboxylic acid (or a salt), an alkaline silicate and a triazole derivative;

- US 2,832,742, for an inhibitor comprising a C_7-C_{18} carboxylic acid and p-tert-butylbenzoic acid;
- US 4,759,864, for an antifreeze comprising a C_6-C_{12} acid or a salt, an alkaline derivative of boron and a triazole derivative.

The publication of G.T.Hefter et al."Organic Corrosion Inhibitor in Neutral Solutions" published in "Corrosion-Vol.53, n° 8, 1997, NACE International" pages 657-667, takes stock of the problems met with in multimetal corrosion.

However, in any case, these compositions do not provide a satisfactory solution to the problem of cavitation corrosion, which remains a major preoccupation, in particular for manufacturers of automobile engines. The compositions of the present invention provide an answer to this problem, which is expressed in practice in their conformity to the requirements of the so-called "cavitation" test, at the same time as those of the standard tests for evaluating the inhibiting effectiveness under hot conditions with respect to various metals in an antifreeze liquid. The CEC C-05X-95 "cavitation" test is that which provides an evaluation of the performance of an inhibiting combination with regard to the corrosion of steel and of aluminium by cavitation of a possibly antifreeze fluid circulating in a loop under standard flow rate, temperature and pressure conditions. These tests are described in the examples.

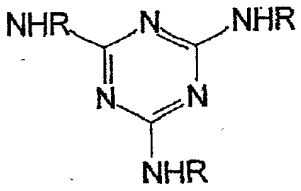
The present invention is that of a process for inhibiting multimetal corrosion by heat transfer fluids, whether or not they comprise an organic compound which lowers the freezing point, which consists in introducing, into the said heat transfer fluids, 3 to 6% by weight and preferably 3,8 to 5% of a system of organic inhibitors composed of:

- (I) 5 to 15% by weight, of at least one unsaturated monocarboxylic acid comprising 10-18 carbon atoms or of one of its alkali metal salts, one of its amine salts, the amine being from the group of monoethylamine, diethylamine or triethylamine, or one of its alkanolamine

salts, the alkanolamine being from the group of monoethanolamine, diethanolamine, triethanolamine or methyldiethanolamine;

- (II) 40 to 70% by weight, of at least one saturated carboxylic acid taken from the group comprising saturated monocarboxylic acids comprising 5-16 carbon atoms and saturated dicarboxylic acids comprising 4-12 carbon atoms or an alkali metal or amine or alkanolamine salt of these acids;

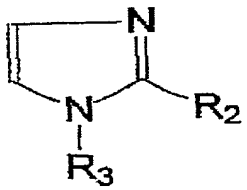
- (III) 20 to 40% by weight, of a tricarboxylic derivative of 1,3,5-triazine corresponding to the formula



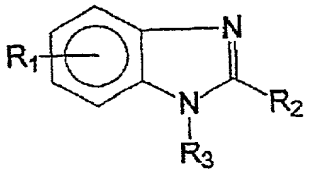
in which formula R is a carboxyalkyl group comprising 2-6 carbon atoms, or an alkali metal or amine or alkanolamine salt of this derivative;

- (IV) 1 to 5% by weight of an azole derivative taken from the group consisting of:

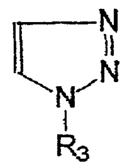
(a) imidazoles of formula



(b) benzimidazoles of formula



(c) triazoles of formula



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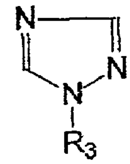
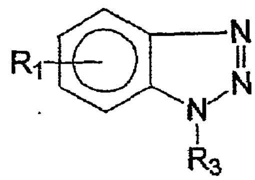
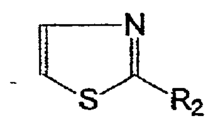


(d) benzotriazoles of formula

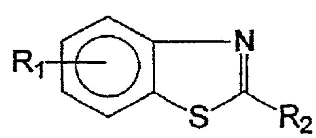


(e) tetrahydrobenzotriazole

(f) thiazoles of formula



(g) benzothiazoles of formula



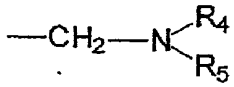
(h) and the alkali metal salts of these azole derivatives,

in which formulae

R1 is a hydrogen atom or a methyl radical

R2 is a hydrogen atom or a mercapto radical

R3 is a hydrogen atom or a radical of formula



with R4 and R5, which are identical or different, representing a 2-ethylhexyl or hydroxyalkyl radical, in particular an ethanol residue.

In a preferred form for using the process of the invention, the ratio by weight of components (I) and (II) (I/II) will range from 5 to 15 and, preferably from 8 to 12, and the ratio by weight of components (I) and (II)on one part and of the component (III) on the other part, (I+II/III), will range from 1,5 to 3 , preferably from 1,9 to 2,2.

Concerning the salts of organic acids the percentages by weight are calculated in relation to the acid fraction of these salts.

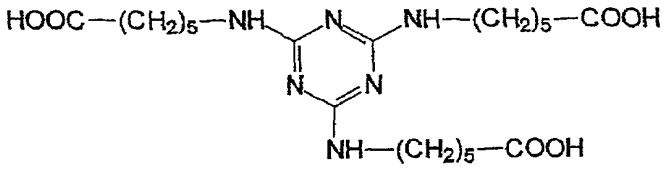
Preference is given, among saturated C5-C16 monocarboxylic acids, to C5-C10 acids, in particular n-hexanoic acid, heptanoic acid, n-octanoic acid and nonanoic acid.

Preference is given, among aliphatic dicarboxylic acids comprising saturated C4-C12 chains, to C4-C10 acids, in particular suberic acid, azelaic acid and sebacic acid.

Preference is given, among unsaturated C10-C22 monocarboxylic acids, to undecylenic acid.

When a saturated monocarboxylic acid and a saturated dicarboxylic acid are used together, it is advantageous to combine them in a diacid/monoacid ratio by mass of 0.1:1 to 10:1, preferably 0.6:1 to 5:1.

The preferred tricarboxylic derivative of 1,3,5-triazine is the compound of formula:



RN = 80584-91-4

or its triethanolamine salt.

The inhibitor system according to the invention can be used in aqueous fluids, with or without antifreeze, for cooling circuits and in particular for cooling circuits of internal combustion engines. It can be employed by directly introducing the different components of the inhibitor system directly into the transfer fluid. It is more convenient to employ mother solutions, which are aqueous solutions comprising from 10 to 60% by weight of the inhibitor system composed of the components (I), (II), (III) and (IV) as described above, for which the pH will be adjusted by neutralizing for instance with caustic soda, to make soluble the whole components, and in such a way as the pH of the transfer fluid will range from 7 to 9, preferably from 7.5 to 8.5. These aqueous mother solutions are compositions of the invention. If it is desired to simultaneously obtain protection of the circuits against corrosion and freezing, use will instead be made of inhibiting antifreeze compositions, also subject-matters of the present invention, composed of:

- 0.1 to 10% by weight of the inhibiting composition described above;
- 90 to 99.9% by weight of an aqueous/alcoholic solution having a freezing point of less than 0°C, preferably of between -10 and -40°C, the alcohol being taken from the group consisting of methanol, ethanol, 2-propanol, glycerol, ethylene glycol, diethylene glycol, propylene glycol, 1-methoxy-2-propanol, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether and ethylene glycol butyl ether. Ethylene glycol is preferred.

The system of inhibitors according to the invention provides protection against multimetal corrosion under cavitation corrosion conditions (high temperature, high pressure) and a fortiori under milder conditions of aggressiveness.

The system of inhibitors according to the invention can be used in a vast range of applications, involving different metals such as ferrous iron, cast iron, cuprous copper,and aluminium especially. Among

these can be cited surface treatment, metal working, paint stripping,lubricating.

EXAMPLES

The examples which follow will make the invention better understood. They require the results of tests regularly carried out in the automobile industry, which tests are restated here:

- a) The corrosion test in glassware (ASTM Standard D 1384: "Corrosion test for Engine Coolants in Glassware"), which makes it possible to monitor the variations in weight of different metals (copper, solder, brass, steel, cast steel, cast aluminium) after immersion for 336 hours (15 days) at 88°C in a corrosive aqueous medium to which antifreeze has been added;

- b) Hot plate test (ASTM Standard D 4340: "Corrosion of cast aluminium alloys in Engine Coolants under Heat-rejecting Conditions"), by which the variations in weight are monitored of a sample made of cast aluminium, simulating a piston, heated at 135°C for 168 hours (7 days) and subjected to a pressure of 193 kPa in a corrosive solution (0.165 g/l of NaCl) comprising 25% of antifreeze;

- c) Cavitation test (CEC Standard C-05X-95), by which the variation in mass is measured of test bodies composed of discs made of cast steel and cast aluminium subjected to the action of the circulating flow of a corrosive solution according to ASTM Standard D 1384 (Na_2SO_4: 148 mg/l, NaCl: 165 mg/l, $NaHCO_3$: 138 mg/l) under test conditions generating differences in local speed and local pressure and in temperature likely to induce cavitation and corrosion phenomena. The temperature of the test is 115°C, the flow rate of the fluid 300 l/h and the pressure 150 kPa. The duration of the test is 72 hours.

The tests take into consideration three types of inhibitors:

i) conventional inorganic compositions based on nitrites, on borax or on sodium molybdate,

ii) organic or mixed compositions of the prior art comprising sebacic acid,

iii) compositions according to the invention.

For all the test compositions, the inhibitor components were dissolved in ethylene glycol. The pH of the concentrated solution was adjusted to between 7 and 8 by addition of sodium hydroxide. The alkaline reserve (AR) of these compositions, expressed in millilitres of 0.1N hydrochloric acid, is determined according to ASTM Standard D 1121-93. These concentrated solutions constitute the antifreezes. The cooling liquids are obtained by dilution to 50% with deionized water. The test solution is composed of a corrosive solution to which this cooling liquid has been added in a proportion of 33% by volume, if ASTM Standard D 1384 is applied, 25% by volume for ASTM Standard D 4340 or 20% by volume for CEC Standard C-05X-95.

Use was made, in preparing the compositions given in the examples, of:

- heptanoic acid (C7) as monocarboxylic acid of type (I),
- undecylenic acid (C11:1) as monocarboxylic acid of type (II),
- the compound Irgacor® L190, sold by Ciba (L190; RN=80584-91-4), as tricarboxylic derivative of triazine,
- tolyltriazole (TTZ) as triazole derivative.

EXAMPLE 1:

The following compositions were prepared as % by weight with respect to the composition in ethylene glycol, the compositions V9 and V10 being preferred compositions according to the invention; the compositions V2, V3 and V6 being outside the invention:

	COMPOSITION					
Component	V2	V3	V6	V8	V9	V10
C7	-	3	3	2	2.5	2.5
C11:1	-	-	-	0.2	0.3	0.3
L190	2	-	1	1	1	1.5
TTZ	0.1	0.2	0.2	0.1	0.1	0.1

The results in the various tests according to the standards related to below are given in the Table 1 .

- For ASTM D1384 (corrosion in glassware), the test is successfully passed if the loss in weight is less than 5 mg with respect to copper, 5 mg with respect to brass, 5 mg with respect to solder, 2.5 mg with respect to steel, 4 mg with respect to cast iron and 10 mg with respect to aluminium.

- The ASTM D4340 test (hot plate) is passed if the loss in weight is less than 1 mg/cm2/week.

- The CEC C-05X-95 test is regarded as acceptable if the variation in weight is between -50 and +10 mg for aluminium and between -10 and +5 mg for cast iron.

TABLE 1

		COMPOSITION					
Test	Specifications	V2	V3	V6	V8	V9	V10
ASTM D 1384							
Copper	-5 mg	-2,1	-0,1	-0,2	-0,4	-0,4	-0,2
Brass	-5 mg	-2,0	-0,1	-0,7	-0,5	-0,5	-0,4
Solder	-5 mg	-6,0	-4,0	-9,3	-44,4	-5,0	-5,0
Steel	-2 mg	-3,5	-2,0	-1,0	-0,2	-0,2	-0,1
Cast steel	-4 mg	-4,7	-2,8	-1,0	-0,5	-0,5	-0,4
Cast Al.	-10 mg	-9,0	-8,0	-1,5	-0,3	-0,4	-0,3
ASTM D 4340							
Cast Al.	-1 mg/cm²/week	-2,5	-1,1	-0,2	-0,4	-0,3	-0,1
CEC C-05X-95							
Cast Al.	-50 +10 mg	-275	-240	-140	-55	-49,2	-45,0
Cast steel	-10 +5 mg	+65	-14	+12	+8	+0,9	+0,5

it can be seen that only the systems possessing four inhibitor components and possessing these components within the limits of the claimed compositions pass all the tests. In particular, it is seen how difficult it is to pass the cavitation test.

EXAMPLE 2 (Comparative): compositions of the prior art

These are organic (O) or organic/inorganic (I) compositions, with diacids (adipic (H2C6) and sebacic (H2C10)), octanoic acid (C8), sodium molybdate (Molyb.), sodium nitrite (Nitrite) and tolyltriazole (TTZ), comprising (as % by weight):

	COMPOSITION			
Component	O1	O2	O3	I1
C_8	2	-	-	-
H_2C_6	-	1	-	-
H_2C_{10}	1.5	3.5	4.25	4.5
Molyb.	-	-	-	0.25
Nitrite	-	-	-	0.25
TTZ	0.1	0.1	0.25	0.1

The results of the tests are given in the Table 2 hereinbelow:

TABLE 2

		COMPOSITIONS			
Test	Specifications	O1	O2	O3	I1
ASTM D 1384					
Copper	-5 mg	-1,5	-2,2	-2,2	-2,0
Brass	-5 mg	-1,7	-2,0	-1,8	-1,5
Solder	-5 mg	-10,2	-15	-2,1	-4,2
Steel	-2 mg	-0,5	-0,4	-0,2	-0,1
Cast steel	-4 mg	-0,9	-0,7	+0,5	-0,5
Cast Al.	-10 mg	-5,0	-7,1	-3,2	-3,0
ASTM D 4340					
Cast Al.	-1mg/cm^2/week	-0,5	-1,0	-0,1	-0,2
CEC C-05X-95					
Cast Al.	-50 +10 mg	-150	-275	-44	-48,0
Cast steel	-10 +5 mg	+4	-20	+2,6	+2,0

Of all these formulae according to the prior art, only the entirely inorganic composition passes all the tests, but with banned or highly inadvisable components. It can be also observed that the

composition O3 gives outstanding results except for the ASTM Standard D 4340 test for the cast steel, in which it gives a weight increase (instead of a loss).This weight increase is a contra-indication for a potential plugging of circuits.

It is well known by one of ordinary skill in the art to blend some complementary additives with this type of formulation to provide specific properties. Among the most standard products, there are antifoaming agents, sequestering agents and colouring agents.

Among the commercial antifoaming agents, the following products are particularly suitable for the claimed composition:

- Wacker SE 47 (silicone based surfactant)
- Pluronic PE6100 sold by BASF (non-ionic surfactant)
- Ultra MS 455-3A (blend of one silicone surfactant and one non-ionic OP-OE).

These products are generally used at the rate of between 0,01 and 0,03% by weight of the formulation of mother solutions.

Among the sequestering agents, a well adapted product to the formulations is 1-hydroxyethane-1,1 diphosphonic acid and particularly the commercial product DEQUEST 2010 of the Company SOLUTIA. This product can present some activity with regard to the corrosion tests, that can involve an arrangement of the global composition according to the invention.

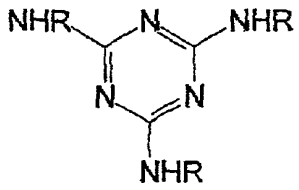
CLAIMS

1. Process for inhibiting multimetal corrosion by heat transfer fluids, whether or not these fluids comprise an organic compound which lowers the freezing point, which consists in introducing, into the said fluids, 3 to 6% by weight and preferably 3,8 to 5% of a system of organic inhibitors composed of:

- (I) 5 to 15% by weight of at least one unsaturated monocarboxylic acid comprising 10-18 carbon atoms or of one of its alkali metal salts, one of its amine salts, the amine being from the group of monoethylamine, diethylamine or triethylamine, or of its alkanolamine salts, the alkanolamine being from the group of monoethanolamine, diethanolamine, triethanolamine or methyldiethanolamine;

- (II) 40 to 70% by weight of at least one saturated carboxylic acid taken from the group comprising saturated monocarboxylic acids comprising 5-16 carbon atoms and saturated dicarboxylic acids comprising 4-12 carbon atoms or an alkali metal or amine or alkanolamine salt of these acids;

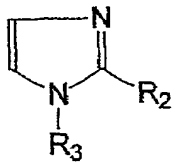
- (III) 20 to 40% by weight of a tricarboxylic derivative of 1,3,5-triazine corresponding to the formula



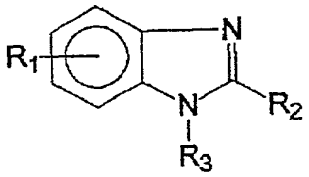
in which formula R is a carboxyalkyl group comprising 2-6 carbon atoms, or an alkali metal or amine or alkanolamine salt of this derivative;

- (IV) 1 to 5% by weight of an azole derivative taken from the group consisting of:

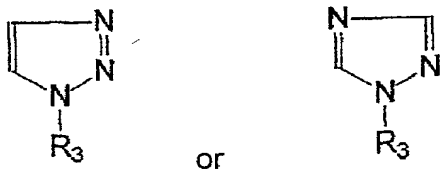
(a) imidazoles of formula



(b) benzimidazoles of formula

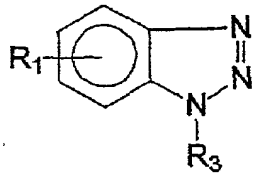


(c) triazoles of formula



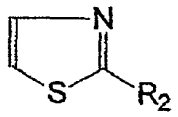
or

(d) benzotriazoles of formula

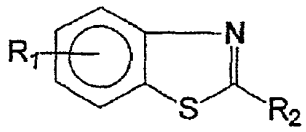


(e) tetrahydrobenzotriazole

(f) thiazoles of formula



(g) benzothiazoles of formula



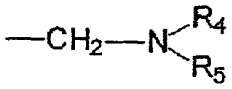
(h) and the alkali metal salts of these azole derivatives,

in which formulae

R1 is a hydrogen atom or a methyl radical

R2 is a hydrogen atom or a mercapto radical

R3 is a hydrogen atom or a radical of formula



with R4 and R5, which are identical or different, representing a 2-ethylhexyl or hydroxyalkyl radical, in particular an ethanol residue.

2. Process according to Claim 1, in which the ratio by weight of components (I) and (II), (I/II), ranges from 5 to 15 and, preferably from 8 to 12, and the ratio by weight of components (I) and (II)on one part and of the component (III) on the other part, (I+II/III), ranges from 1,5 to 3 , preferably from 1,9 to 2,2.

3. Process according to either of Claim 1 and 2, in which the system of organic inhibitors is composed of:

- 6 to 8% by weight of the component(I);

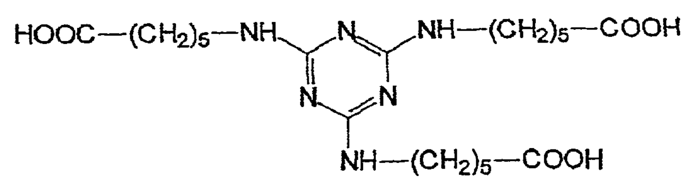
- 55 to 65% by weight of the component (II);
- 25 to 35% by weight of the component (III);
- 2 to 3% by weight of the component (IV).

4. Process according to either of Claims 1 to 3, in which the saturated carboxylic acid is n-hexanoic acid, heptanoic acid, n-octanoic acid or nonanoic acid.

5. Process according to either of Claims 1 to 3, in which the dicarboxylic acid is suberic acid, azelaic acid or sebacic acid.

6. Process according to either of Claims 1 to 3, in which the unsaturated monocarboxylic acid is undecylenic acid.

7. Process according to either of Claims 1 to 3, in which the tricarboxylic derivative of 1,3,5-triazine is the compound of formula:



8. Composition which inhibits multimetal corrosion, composed of an aqueous solution assaying from 10 to 60% by weight of an inhibitor system as described in Claims 1 to 7.

9. Antifreeze composition which inhibits multimetal corrosion, comprising:

- 0.1 to 10% by weight of the inhibiting composition according to Claim 8;
- 90 to 99.9% by weight of an aqueous/alcoholic solution having a freezing point of less than 0°C, preferably of between -10 and

-40°C, the alcohol being taken from the group consisting of methanol, ethanol, 2-propanol, glycerol, ethylene glycol, diethylene glycol, propylene glycol, 1-methoxy-2-propanol, ethylene glycol methyl ether, ethylene glycol ethyl ether, ethylene glycol propyl ether and ethylene glycol butyl ether.

10. Inhibiting antifreeze composition according to Claim 9, the alcohol of which is ethylene glycol.

ABSTRACT

CORROSION-INHIBITING COMPOSITIONS FOR HEAT TRANSFER FLUIDS

A description is given of compositions which inhibit the corrosion of many metals by heat transfer fluids, which are composed of the combination of an unsaturated monocarboxylic acid, of a saturated mono- or dicarboxylic acid, of a tricarboxylic derivative of 1,3,5-triazine and of an azole derivative. These compositions in particular inhibit cavitation corrosion.

Attorney Docket Number: ATOCM 241

DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

CORROSION INHIBITING COMPOSITIONS FOR HEAT TRANSFER FLUIDS

the specification of which

- ☐ is attached hereto
- ■ was filed on 23 JUNE 2000 as United States Application Number or PCT International Application Number PCT/FR00/01760 and (if applicable) was amended on _____

I hereby authorize our attorneys to insert the serial number assigned to this application.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

PRIOR FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 USC §119			
APPLICATION NO.	COUNTRY	DAY/MONTH/YEAR FILED	PRIORITY CLAIMED
99/08214	FRANCE	28 JUNE 1999	YES

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below.

PROVISIONAL APPLICATION(S) UNDER 35 U.S.C. §119(e)	
APPLICATION NUMBER	FILING DATE

I hereby claim the benefit under 35 U.S.C. §120 of any United States application, or §365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. §112.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR §1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

PRIOR U.S./PCT INTERNATIONAL APPLICATION(S) DESIGNATED FOR BENEFIT UNDER 37 U.S.C. §120		
APPLICATION NO.	FILING DATE	STATUS — PATENTED, PENDING, ABANDONED

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected herewith: I. William Millen (19,544); John L. White (17,746); Anthony J. Zelano (27,969); Alan E.J. Branigan (20,565); John R. Moses (24,983); Harry B. Shubin (32,004); Brion P. Heaney (32,542); Richard J. Traverso (30,595); John A. Sopp (33,103); Richard M. Lebovitz (37,067); John H. Thomas (33,460); Catherine M. Joyce (40,668); Nancy J. Axelrod (44,014); James T. Moore (35,619); James E. Ruland (37,432); Jennifer J. Branigan (40,921) and Robert E. McCarthy (46,044)

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☐ Additional joint inventors are named on separately numbered sheets attached hereto.